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Published in:
Physical Review Letters

Link to article, DOI:
10.1103/PhysRevLett.46.852

Publication date:
1981

Document Version
Publisher's PDF, also known as Version of record

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Zero-Pressure Organic Superconductor: Di-(Tetramethyltetraselenafulvalenium)-Perchlorate [$(TMTSF)_2ClO_4$]

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(Received 29 December 1980)

Evidence for superconductivity in the organic conductor di-(tetramethyltetraselenafulvalenium)-perchlorate [$(TMTSF)_2ClO_4$] has been found by resistance measurements in the absence of applied pressure. For different crystals the transitions are approximately 0.3 K wide and are centered around temperatures between 1.2 and 1.4 K. At 0.9 K, a perpendicular magnetic field of 25 mT nearly restores normal resistance. Below 0.1 K, this critical field exceeds 50 mT.

PACS numbers: 74.10.+v

The recent observations of superconductivity in some organic crystals of the type $(TMTSF)_2X$ under pressure[1-4] have added empirical substance to the continuous theoretical debate about the occurrence of superconductivity in organic, quasi-one-dimensional materials.[5-8] For instance, crystals of di-(tetramethylselenafulvalenium)-hexafluorophosphate $(TMTSF)_2PF_6$ become superconducting at pressures above $P = 0.6$ GPa (6 kbar)[1-3] with a pressure-dependent critical temperature $T_c \lesssim 1.3$ K. However, since pressure often has the effect of suppressing other instabilities,[9] e.g., the Peierls instability leading to a metal-insulator transition, the question is if pressure is necessary to provide circumstances leading to superconductivity. In this paper we present evidence from resistance measurements that crystals of di-(tetramethyltetraselenafulvalenium)-perchlorate [$(TMTSF)_2ClO_4$] exhibit superconductivity in the absence of applied pressure.

$(TMTSF)_2ClO_4$ belongs to the family of organic cation radical salts $(TMTSF)_2X$,[10] where X is an anion of high symmetry. High-quality crystals of this compound were obtained by electrochemical oxidation in 1,1,2-trichloroethane containing the electrolyte n-Bu_4NClO_4.[11] We have studied crystals from three different batches, grown under different conditions.

The idea behind changing the anion X from the octahedral anion PF_6^- to the tetrahedral ClO_4^- ion is that the latter is smaller, which might have the same effect on the conducting TMTSF stacks as pressure has in $(TMTSF)_2PF_6$. This expectation is fulfilled since the structural analysis shows that the two compounds are isostructural with a unit-cell volume of $V = 694.3$ Å^3 and $V = 714.3$ Å^3 when $X = ClO_4^-$ and PF_6^-, respectively.[11,12] Actually this contraction corresponds to

a pressure of about 0.3 GPa on $(TMTSF)_2PF_6$, assuming the same compressibility as for another TMTSF compound, TMTSF-DMTCNQ.[13] Another interesting structural feature is that the ClO_4^- ions appear to be disordered (see Fig. 1), whereas PF_6^- is ordered.

Our samples were single crystals of typical dimensions $4\times0.2\times0.2$ mm^3. For four-terminal resistance measurements four gold wires were silver-pasted approximately 1 mm apart along the needle. The resistance R was measured by continuously recording the voltage caused by a low-frequency current of constant amplitude. Measurements from room temperature to 4.2 K, and from 4.2 to 12 mK, were performed separately. In the latter temperature range the crystals were immersed in liquid in the mixing chamber of a dilution refrigerator.

The resistivity $\rho(T)$ for $(TMTSF)_2ClO_4$ between 1 and 293 K is shown in Fig. 1. The room-temperature resistivity is 1.5×10^{-5} Ω m, taken as an average for six crystals, where the dimensions have been carefully measured. Deviations from this mean value of ρ(293 K) could be accounted for by the uncertainty in determining the involved lengths. In Fig. 1, data for crystals investigated at low temperatures only have been normalized to fit the high-temperature behavior of crystals for which this was satisfactorily investigated. Between 20 K and room temperature, $\rho(T)$ follows an approximate power law $\rho(T)\propto T^{\lambda}$, where $\lambda\lesssim2$. This is similar to the other $(TMTSF)_2X$ salts,[10] but a slightly weaker temperature dependence than usual for other organic conductors. At temperatures below 10 K, $\rho(T)$ is nearly constant (but sample dependent) until a spectacular drop sets in near 1.3 K. All six crystals investigated below 4.2 K showed this behavior, which we associate with the onset of superconductivity.

In Fig. 2, results near the transition are displayed in more detail for a crystal of batch 3. In this range temperature was measured by means of a calibrated carbon resistor. Data points taken for increasing and for decreasing temperature coincide within the uncertainty. We define a transition temperature T_c by $\rho(T_c)=\frac{1}{2}\rho_n$, where ρ_n is the normal resistance above the transition. T_c appears to depend on the measuring current (Fig. 2) but we ascribe this effect to heating in the current contacts, which can have resistance of the order 10^4 Ω. The magnetic field produced by the sample current is too small for any magnetic ef-

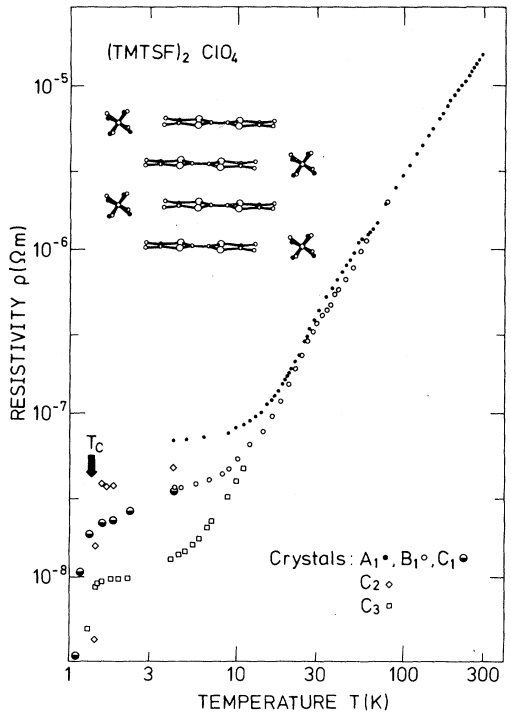

FIG. 1. Temperature dependence of the resistivity $\rho(T)$ for $(TMTSF)_2ClO_4^-$. Results for different crystals have been normalized to the same high-temperature behavior (see text). The inset shows the crystal structure, where the disorder of the ClO_4 ions is indicated by the two orientations occupied with equal probability.

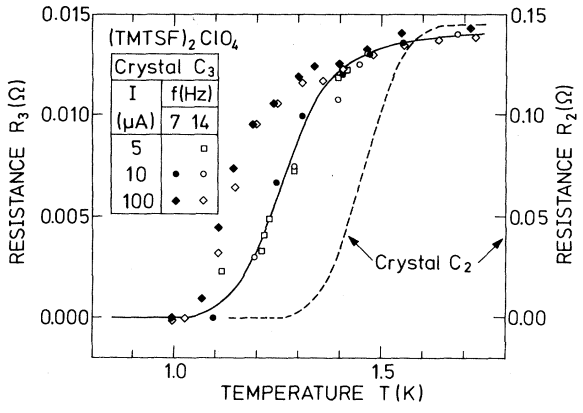

FIG. 2. Temperature dependence of the measured resistance in the vicinity of the superconducting transition shown for different measuring frequencies. The solid line is a guide to the eye through the measured points for crystal C_3 (batch 3) for currents of 10 μA or less, where heating effects can be neglected. The dashed line shows corresponding results for crystal C_2 (batch 2). The apparent decrease in T_c for C_3 at 100 μA is considered to be caused by local heating.

fects on T_c to be conceivable, but the point needs further investigation. Several crystals showed this "heating effect," but to a different extent. Crystal C_1 (Fig. 1) was investigated only at a relatively high current (70 μA).

Heating effects cannot explain, however, the difference in T_c between samples C_2 (batch 2, T_c = 1.46 K) and C_3 (batch 3, T_c = 1.26 K), demonstrated in Fig. 2, since both samples were here investigated in the low-current limit. Hence the transition in $(TMTSF)_2ClO_4$ appears to be influenced by imperfections (e.g., impurities or defects) which may vary from batch to batch. Further, an inhomogeneous distribution of such imperfections in a crystal would also explain why the transition is broad.

Figure 3 shows the effect on R when a magnetic field is applied perpendicularly to the conducting axis of the crystal C_3. It shows that, as the temperature is lowered through T_c, a critical field of increasing strength is needed to restore the normal state, a characteristic feature of a superconductor. At T = 0.91 K we find the critical field $B_\perp$ = 25 mT (250 G). At T = 1.35 K, i.e., above T_c, where the resistance is already close to ρ in the absence of a field, only a small induction of $B_\perp \approx 3$ mT is needed to recover ρ_n. It should be noted that superconductivity persists in these crystals to temperatures 0.2–0.3 K above T_c defined above, in the sense that a magnetic field causes resistance to increase, until ρ_n is reached. At temperatures higher than T_c + 0.3 K, magnetoresistance is unmeasurably small at our highest field, 75 mT.

With our ac method we had the problem that the recorded voltage along the crystal had a finite value below the transition. This residual, temperature-independent voltage typically amounted to 10% of the voltage due to the normal resistance. By varying the sample current and frequency of measurement, we could separate the linear resistance of the sample from the strongly nonlinear contribution from the residual voltage which we therefore ascribe to artifacts associated with the contact impedances.[14] Contacts are known to be difficult to preserve during cooldown, and this problem is worse when the sample *is not* enclosed in a pressure cell, which leads to the paradoxical situation that a zero-resistance state is more difficult to measure at ambient pressures. In Figs. 2 and 3 the residual voltage was subtracted before calculation of resistance. As a result we are able to set an upper limit of $0.03\rho_n$ to the resistivity well below T_c.

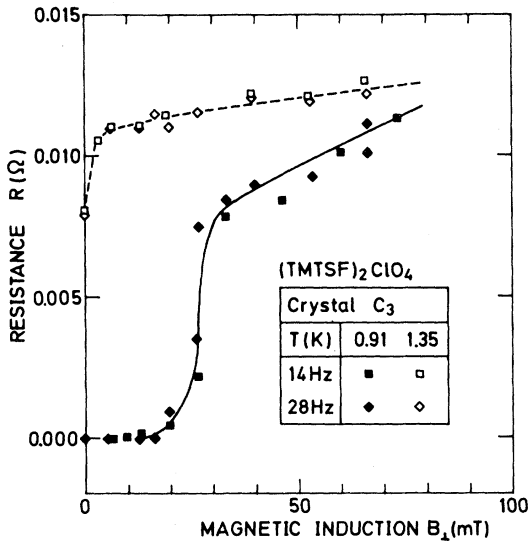

FIG. 3. Effects of a transverse magnetic field $B_\perp$ on the sample resistance of crystal C_3 at temperatures 0.91 K and 1.35 K.

Properties of a given crystal as displayed in Figs. 2 and 3 reproduced well in a second cooldown after warming to liquid-nitrogen temperature.

The transition temperature observed here for $(TMTSF)_2ClO_4$ is comparable to the transition temperature observed in $(TMTSF)_2PF_6$ under sufficient pressures. For the latter material, one group[3] has observed broad transitions similar to those reported here, while another group finds considerably sharper transitions.[1] Pressure studies, consistent with our findings, are being carried out on $(TMTSF)_2ClO_4$.[15]

In conclusion, we have observed the first evidence for superconductivity in an organic material without application of pressure. Further studies are needed to fully characterize the state below T_c. The relatively high T_c, and the fact that pressure is not needed, make $(TMTSF)_2ClO_4$ an excellent material for the study of superconductivity in organic materials.

This work was supported by the Danish Natural Science Research Council.

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Effect of Configuration Crossover on the Electronic Raman Scattering by 4*f* Multiplets

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The effect of configuration crossover on excited $4f^6(^7F_J)$ levels has been investigated by electronic Raman scattering in $Sm_{1-x}Y_xSe$ and $Sm_{1-x}Y_xS$. The multiplet levels are wiped out when they merge with the conduction band, or when interacting with phonons. Polarized Raman-scattering data on $Sm_{1-x}Y_xS$ for $x > 0.15$ show that the contribution from J-multiplet levels is unobservable and that the peak near 250 cm^{-1} arises from optic phonons and not from $J = 0 \rightarrow J = 1$ excitations.

PACS numbers: 78.30.Gt, 71.30.+h, 71.70.Ms

The anomalous features of the intermediate valence state of rare earth ions in solids arise from the degeneracy of nominally two 4*f* configurations. From previous Raman[1] and neutron studies[2] on SmS and $Sm_{1-x}Y_xS$ it is believed that the ionic character of the original 4*f* configuration is still preserved at configuration crossover (CC) and beyond, and that a Hund's rule description is still valid. On this basis the lifetime broadening of excited 4*f*-multiplet levels due to mixing with conduction-electron states has been predicted theoretically.[3]

In this Letter we show for the first time and convincingly by means of Raman scattering that the 4*f*-multiplet structure is strongly affected near CC and becomes unobservable by Raman scattering beyond CC. The Raman feature observed[1] near 250 cm^{-1} in $Sm_{1-x}Y_xS$ for $x > 0.15$ (beyond CC), exhibiting a clear-cut polarization characteristic opposite to that associated with the electronic $J = 0 \rightarrow J = 1$ excitation of Sm^{2+}, is due to optical phonons. In this connection we have carried out Raman-scattering experiments on $Sm_{1-x}Y_xSe$, $Sm_{1-x}Y_xS$, and $Sm_{1-x}Gd_xS$ near, at, and beyond CC. We first establish the polarization selection rules for the electronic Raman scattering arising from the J multiplets by studying pure SmSe and SmS, and then show how these

